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RARE-EARTH PENTAPHOSPHATES FOR MINIATURIZED LASER APPLICATIONS.(U)
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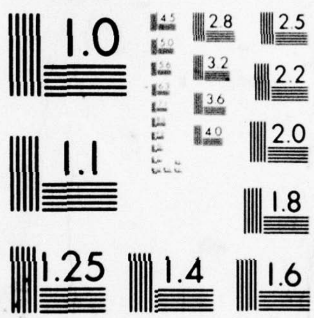

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RARE-EARTH PENTAPHOSPHATES FOR MINIATURIZED LASER APPLICATIONS

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February 1977

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Neodymium pentaphosphate (NdPP) has recently emerged as a new laser compound offering a considerable improvement in operating efficiency over existing materials. Up to thirty times more Nd can be incorporated than in Nd:yttrium aluminum garnet, without substantial fluorescence quenching, linewidth broadening, lifetime reduction and optical degradation of the crystal. The evaluation and testing of NdPP lasers in prototype components using optical pumping has been hindered due to the limited size, availability and quality of the single crystals.

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20. Abstract (cont'd)

Unique modifications of conventional solution growth techniques have been devised which have yielded the largest crystals (greater than 1 cm) of NdPP currently available. Ambient control, growth temperature, rare-earth oxide to phosphoric acid ratio, and seeding were found to greatly influence nucleation, growth rate and crystal quality. An as-grown crystal of NdPP containing 10 percent yttrium, 2.5 x 3.5 x 2.2 mm thick, produced 0.24 watts of output power for 1.0 watt of absorbed power using longitudinal pumping with a repetitively pulsed argon laser; the conversion efficiency is approximately 24 percent.

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RARE-EARTH PENTAPHOSPHATES FOR MINIATURIZED LASER APPLICATIONS

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INTRODUCTION

The requirement for low-threshold high-efficiency laser sources for miniaturized rangefinder and fiber optic communication applications has led to the study of rare earth pentaphosphate compounds. Neodymium pentaphosphate (NdPP) has recently emerged as a promising 1.05 μm laser material (1-3) operating in pulsed and cw modes, with thresholds of the latter reported less than 1 milliwatt (4). In contrast to doped lasers such as Nd:YAG, NdPP is a stoichiometric compound (NdP_5O_{14}) which accommodates up to thirty times more Nd than YAG. The evaluation and testing of NdPP lasers in prototype components using transverse and longitudinal optical pumping has been hindered due to the limited size (several mm), availability, and quality of the single crystals. We have devised unique modifications of conventional solution growth techniques in order to control reaction kinetics and precipitation rates. The largest bulk single crystals (> 1 cm) of yttrium and lanthanum substituted NdPP presently available were grown by these modified techniques. We have observed laser action in as-grown 90% Nd 10% Y pentaphosphate crystals with dimensions typically 4.5×3 mm in diamond-shaped cross section by 2 mm thick. Power conversion efficiencies of ∿ 24% and peak power outputs of approximately 240 milliwatts were obtained under optical excitation with a repetitively pulsed argon laser.

NdPP was the first neodymium compound to exhibit stimulated emission and was observed and reported by Weber et al in 1973 (5). This disclosure generated considerable interest because of the high Nd

concentration possible (4×10^{21} atoms/cc compared to 1.4×10^{20} atoms/cc for Nd: YAG) without substantial fluorescence quenching, lifetime reduction, linewidth broadening, and optical degradation of the crystal. These unique properties of NdPP have been suggested as being the result of: a) the large nearest neighbor Nd-Nd separation of 5.2 Å which reduces Nd^{3+} dipole-dipole interactions (in YAG the Nd ion separation can be as small as 3.7 Å); b) a favorable position of the $^4I_{15/2}$ manifold relative to the upper laser state $^4F_{3/2}$ and the ground state $^4I_{9/2}$; c) the fact that neodymium is an integral component of the basic pentaphosphate compound, permitting complete filling of the available sites with Nd; and d) isolation of the Nd ions from their nearest Nd neighbors by the configuration of the Nd-O polyhedra.

In projecting the use of NdPP in miniaturized laser applications, several advantages over existing materials are apparent. The Nd concentration can be varied over wide limits in pentaphosphates ($\sim$ 0 to 100%), by dilution with inert cations such as those of Y and La; this allows, for the first time, "molecular engineering" of the chemical composition for a specific pump band absorption strength. Uniform pumping of, and maximum absorption by the lasing medium is of paramount importance, since the efficiency of a laser is directly related to the amount of radiation absorbed. An almost twofold increase in pumping efficiency and lower threshold (output coupling greater than 8%) is projected if a 3 x 15 mm Nd:YAG mini-laser rod could be replaced by one of NdPP containing 6.4% Nd. NdPP single-crystal fibers or mini-rods may be useful for higher power 1.05 μm sources for fiber-optic communications, where longer cables without repeaters are envisioned. Compared to present light emitting diodes (LED) or laser diode sources, NdPP lasers would have better mode control, beam divergence, and transmission characteristics when used with current optical fibers.

CRYSTAL GROWTH

The lanthanide series pentaphosphates of the general type LnP_5O_{14} have been prepared by several investigators (3-9) using precipitation from polyphosphoric acid solutions. Synthesis of these compounds is very inexpensive when compared to conventional high temperature Czochralski growth of refractory laser materials such as YAG, YVO_4 and YALO. The pentaphosphates crystallize in two crystal systems, monoclinic and orthorhombic, and exhibit three structure types. One type of monoclinic cell ($P2_1/c$) is formed when large rare earth ions (La thru Tb) are used. The smaller rare earth ions (Tb thru Lu)

produce a different monoclinic structure type (C2/c). The pentaphosphates of Dy, Ho and Er also crystallize in the orthorhombic system (Pnma), along with Y and Bi. By substituting an inert ion such as yttrium for neodymium in the pentaphosphate structure, one may readily vary, for example, the fluorescence lifetime, threshold, absorption coefficient and power output.

The pentaphosphates are prepared by slowly adding the desired rare earth oxide and diluent oxide (if applicable) to orthophosphoric acid at approximately 200°C. After the oxides are added, the crucible is covered and placed in a resistance furnace at temperatures to 600°C. After a period ranging from one to two weeks, the furnace is cooled, the crucible removed and the crystals extracted by leaching the remaining polyphosphoric acid with hot water. Hot phosphoric acid is extremely corrosive and attacks even gold and platinum crucibles at the temperatures used for growth. We have found that vitreous carbon, pyrolytic carbon coated, and pyrolytic silicon carbide coated carbon crucibles are all highly resistant to acid attack and leakproof. Therefore, these were used in place of gold and platinum crucibles.

Although the growth procedure for pentaphosphates is straightforward, the phosphoric acid system is complex. The various condensed phases which can exist in solution depend on the temperature and the partial pressure of the water vapor above the solution. A description of the events we believe occur during formation and crystallization of NdPP from polyphosphoric acid fluxes follows.

Reagent grade orthophosphoric acid, containing 15% water, is heated to approximately 200°C to boil off most of the water. When neodymium oxide is added to an excess of the hot acid, the pentaphosphate is formed with the simultaneous evolution of water. This is indicated by the reaction:

$$10\ H_3PO_4 + Nd_2O_3 \xrightarrow{\sim 200^\circ C} 2\ NdP_5O_{14} + 15\ H_2O\uparrow .$$

As the unreacted phosphoric acid containing the dissolved NdPP is slowly heated above 200°C, further dehydration occurs leading to the formation of pyrophosphoric acid via the reaction:

$$2\ H_3PO_4 + NdP_5O_{14} \xrightarrow{> 200^\circ C} H_4P_2O_7 + NdP_5O_{14} + H_2O\uparrow .$$

NdPP is soluble in pyrophosphoric acid (6) and no precipitation is believed to occur during this transitional phase. As the temperature

is increased above 300°C, dehydration continues with the formation and polymerization of metaphosphoric acid. Since the pentaphosphates have reduced solubility in polymerized metaphosphoric acid, a condition of supersaturation is reached which causes nucleation and subsequent crystal growth to occur as:

$$H_4P_2O_7 + NdP_5O_{14} \xrightarrow{> 300^\circ C} 2(HPO_3)_n + NdP_5O_{14}\downarrow + H_2O\uparrow .$$

In order to obtain bulk crystals of high perfection, it is critical to control precisely the rate at which water and polyphosphoric acid are lost through vaporization. If an open crucible is used, a mass of generally thin platelets of very poor optical quality results in one or two days. Therefore, our efforts were focused on various methods for minimizing loss of the volatile components in order to control the growth process. Also, the following growth variables were studied to ascertain their influence on crystal size, morphology, and perfection:

a) Growth temperature (350 to 600°C)

b) Rare earth oxide to phosphoric acid ratio (0.01 to 0.20 grams/ml)

c) Diluent ions (Y, In, Bi, Gd, Ce, and La)

d) Seeded growth.

Crystals of poor optical quality, containing numerous internal defects, were grown at temperatures of 350 to 450°C. At temperatures of 450 to 600°C the crystals produced were of high optical quality, with temperatures from 525 to 600°C yielding the larger crystals (>1cm). During each growth run, several high optical quality single crystal mini-rods (typically 0.5 mm diameter by 2 mm long) and fibers (0.1 by 2 mm long) were also synthesized. The addition of several seed crystals, a few millimeters in size, was found to reduce greatly the degree of supersaturation. This step led to at least a tenfold reduction in the number of nucleation sites formed, enhancing growth of fewer but larger crystals. Crystals of NdYPP up to 1 cm in size have been grown on rotating seeds at 350 to 400°C, but their quality was generally poorer because of the lower growth temperatures required to prevent rapid vaporization of the polyacid and water.

Initial rare earth oxide to phosphoric acid ratios were found to be directly related to crystal size, yield, and perfection. The

amount of rare earth oxide added determines precisely the concentration of pentaphosphate in the polyphosphoric acid during growth. Ratios of 0.01 to 0.20 grams REO/ml H_3PO_4, corresponding to 0.03 to 0.06 grams REPP/ml of initial phosphoric acid, were investigated. Larger crystals of high quality were consistently grown from the more dilute solutions, 0.015 to 0.030 grams REO/ml H_3PO_4. Concentrations above 0.03 grams REO/ml H_3PO_4 generally led to a higher degree of supersaturation which promoted spontaneous nucleation of many small crystals containing numerous internal defects.

The physical configuration of the crucible and its environment plays an important role in controlling the loss of vapor, which indirectly controls the growth rate. Generally, the slowest rate of evaporation at a given temperature yielded the highest quality single crystals. Conducting growth runs in a sealed system containing a slight overpressure of nitrogen (15 psi) and also in an atmosphere saturated with vapor was of no apparent value in obtaining high quality bulk crystals. The combination of a dilute solution, seeding, growth temperatures of 500 to 600°C, and a double crucible configuration has consistently yielded higher quality and larger single crystals. A diagram of the apparatus and results is shown in Figure 1.

Two crystals of $Nd_{0.9}La_{0.1}P_5O_{14}$ grown at 550°C are shown in Figure 2.

FLUORESCENCE AND LASER PERFORMANCE

As previously mentioned, the fluorescence and laser properties can be modified by varying the amount of inert ions incorporated in the pentaphosphate structure. Y, Ce, Gd, La, In, and Bi were evaluated as diluent ions both in terms of the ease of crystal growth and fluorescent properties. No appreciable difference was observed in growth rate, size, and crystal quality with respect to the diluent ion used. The fluorescent lifetimes of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition were measured to evaluate the influence of various diluent ions. The fluorescent lifetime could be varied by the type and amount of ion added, and some typical values are shown in Table 1.

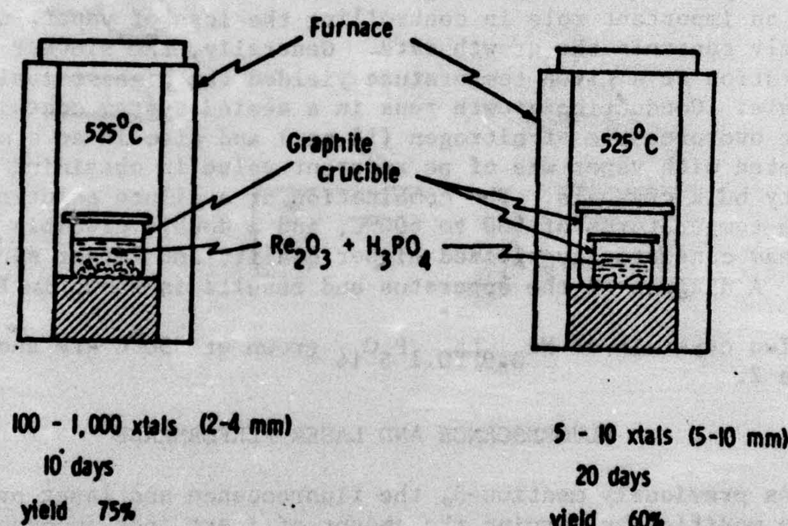
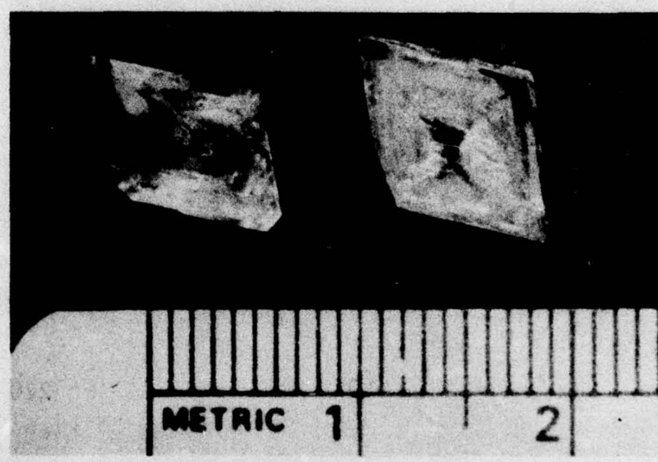


Figure 1. Single and double crucible experimental arrangements for growth of rare earth pentaphosphates, showing typical size and number of crystals, % yield and growth duration.



(a) (b)

Figure 2. Crystals of $Nd_{0.9}La_{0.1}P_5O_{14}$ grown from polyphosphoric acid by (a) free nucleation (4 mm thick) and (b) seeded solution (8.5 mm thick), with seed crystal placed on the bottom of the crucible. (3x)

TABLE 1. ROOM TEMPERATURE FLUORESCENT LIFETIMES OF NEODYMIUM PENTAPHOSPHATE CONTAINING VARIOUS DILUENT IONS

Diluent Ion	Nd Concentration (Mole %)	Fluorescent Lifetime (μsec)
None	100	100
La	trace	300 (Ref. 1)
La	10	195
La	90	110
Y	10	220
Y	90	120
Gd	10	260
Ce	10	270

Single crystals of Nd, Sm, Eu, Tb, Dy, and Er pentaphosphate were grown to determine the spectroscopic properties of these rare earths in the pentaphosphate structure. The various fluorescence peaks, room temperature linewidths and lifetimes, and terminal fluorescence levels of these ions are shown in Table 2. Eu, Tb and Dy pentaphosphates appear to have potential as visible lasers.

TABLE 2. SPECTROSCOPIC PROPERTIES* OF RARE EARTH PENTAPHOSPHATES

Element	Fluorescence (μm)	Linewidth (A)	Lifetime (μsec)	Terminal State (cm^{-1})
Nd	0.885	62		200
Nd	1.052	16	100-300	2000
Nd	1.320	46		4000
Sm	0.595	60	80	1000
Eu	0.612	9	4800	1000
Tb	0.545	13	4000	2000
Dy	0.577	13	342	3000
Dy	0.488	5		416
Er	1.530	2(77°K)		131

*Measurements made at room temperature.

A theoretical study was conducted to determine the amount of available power and optimum output coupling of NdPP for fiber optic applications, using a five element laser diode array as a pump (10). The results are shown in Figure 3.

As seen from Figure 3, a five element 100 milliwatt laser diode array (commercially available) would generate 54 milliwatts of cw output power from NdPP, using an output coupling of ∿ 0.03. This indicates one could readily achieve high output powers from such a configuration for fiber optic applications.

The theoretical incident threshold intensity as a function of nonresonant loss for NdPP and 1% Nd:YAG is shown in Figure 4. A Nd concentration of 6.4% in the pentaphosphate was chosen to obtain uniform pumping (63% absorption per pass) of the crystal (10).

The theoretical threshold power required for NdPP is shown to be lower than that of Nd:YAG, when nonresonant losses are greater than 8%. Current rangefinders and those envisioned operate at considerably

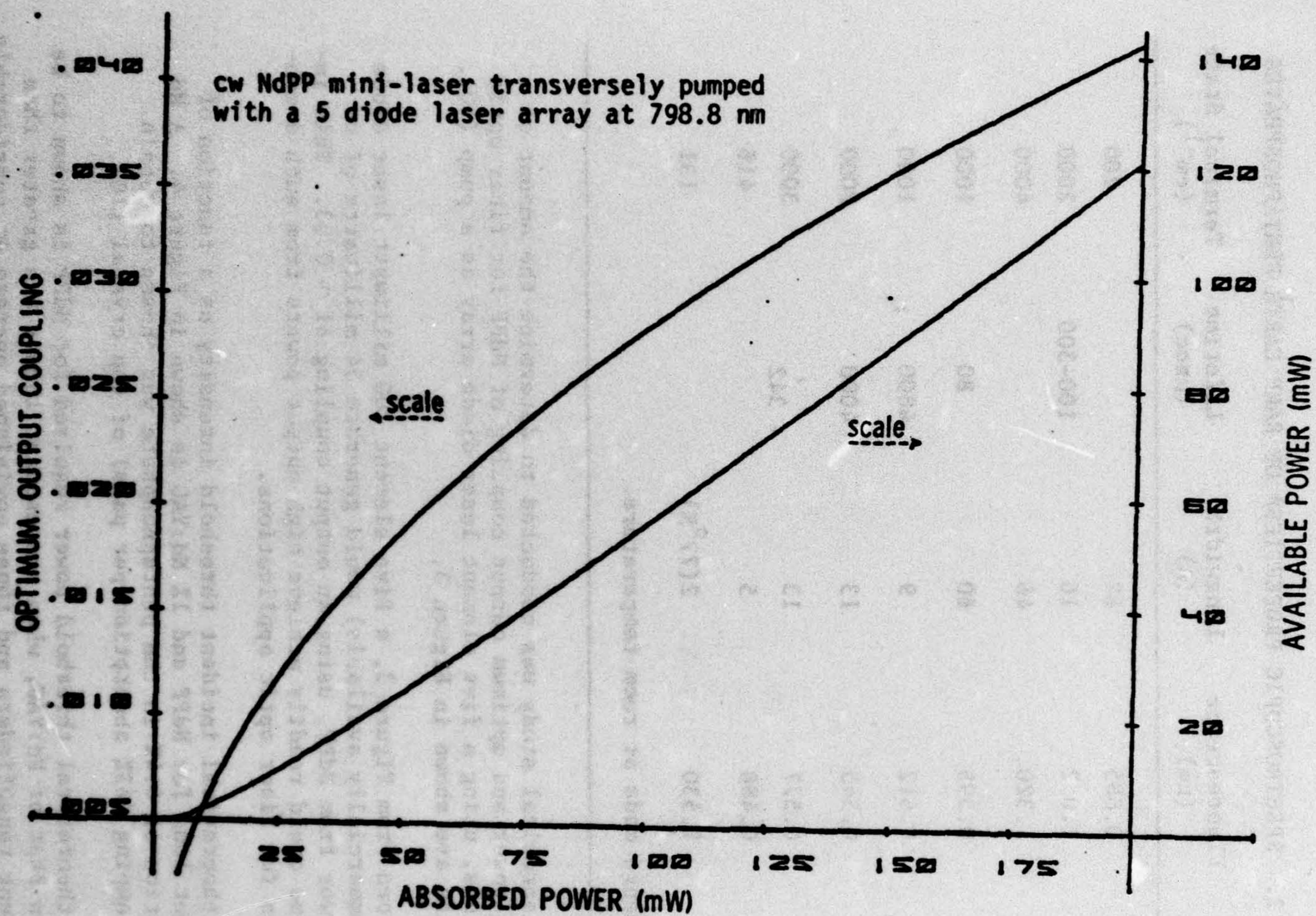


Figure 3. Calculated available cw output power and optimum output coupling as a function of absorbed power, for a 1.0 mm long by 0.08 mm diameter crystal of NdPP.

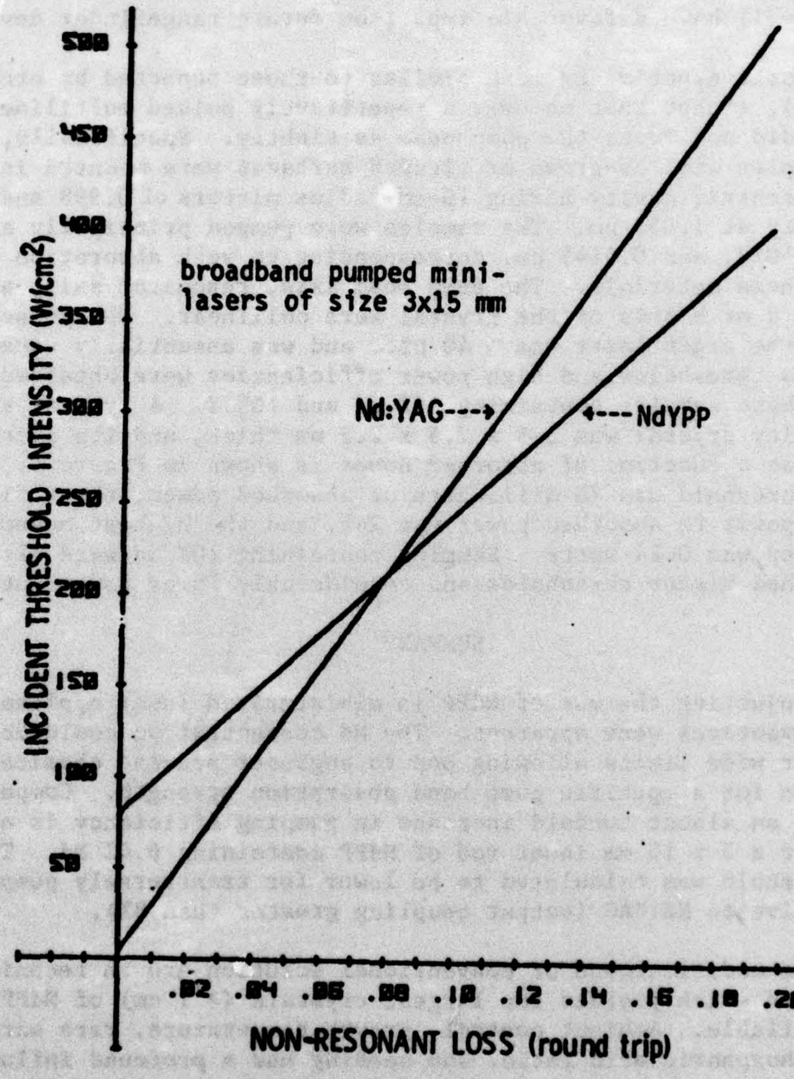


Figure 4. Calculated incident threshold intensity as a function of nonresonant loss for broadband pumped $Nd_{0.064}Y_{0.936}P_5O_{14}$ and 1% Nd:YAG.

higher nonresonant losses; therefore, from these results it is felt that NdPP will have a favorable impact on future rangefinder devices.

Our laser experiments were similar to those reported by others (5, 11, 12), except that we used a repetitively pulsed multiline argon laser and did not focus the pump beam as tightly. Specifically, uncoated samples with as-grown or cleaved surfaces were mounted in a nearly concentric cavity having 10-cm-radius mirrors of 0.998 and 0.980 reflectivity at 1.051 μm. The samples were pumped principally at 0.4765, 0.5017, and 0.5145 μm, corresponding to weak absorption bands of Nd in these materials. The pump beam axis, resonator axis, and either the a or b axis of the crystal were collinear. The pulse length of the argon laser was ∿ 40 μsec and was essentially square in shape. Low thresholds and high power efficiencies were obtained in pentaphosphate samples containing 90% Nd and 10% Y. A typical size laser quality crystal was 3.5 x 2.5 x 2.2 mm thick, and its laser output power as a function of absorbed power is shown in Figure 5. The measured threshold was 70 milliwatts of absorbed power, the efficiency of output power to absorbed power was 24%, and the highest measured output power was 0.24 watts. Samples containing 10% Nd were also lased but had higher thresholds and considerably lower power outputs.

SUMMARY

In projecting the use of NdPP in miniaturized laser applications, several advantages were apparent. The Nd concentration could be varied over wide limits allowing one to engineer precise chemical composition for a specific pump band absorption strength. Compared to Nd:YAG, an almost twofold increase in pumping efficiency is anticipated for a 3 x 15 mm laser rod of NdPP containing 6.4% Nd. The power threshold was calculated to be lower for transversely pumped NdPP relative to Nd:YAG (output coupling greater than 8%).

Unique modifications of conventional solution growth techniques were devised which yielded the largest crystals (> 1 cm) of NdPP currently available. Ambient control, growth temperature, rare earth oxide to phosphoric acid ratio, and seeding had a profound influence on nucleation, growth rate, and crystal quality. An as-grown crystal of NdPP containing 10% yttrium, 2.5 x 3.5 x 2.2 mm thick, produced 0.25 watts of output power, at a power conversion efficiency of 24%. We believe that high efficiency stoichiometric laser compounds such as NdPP, will make a significant impact in providing miniaturized laser sources for next generation rangefinders and fiber optics systems.

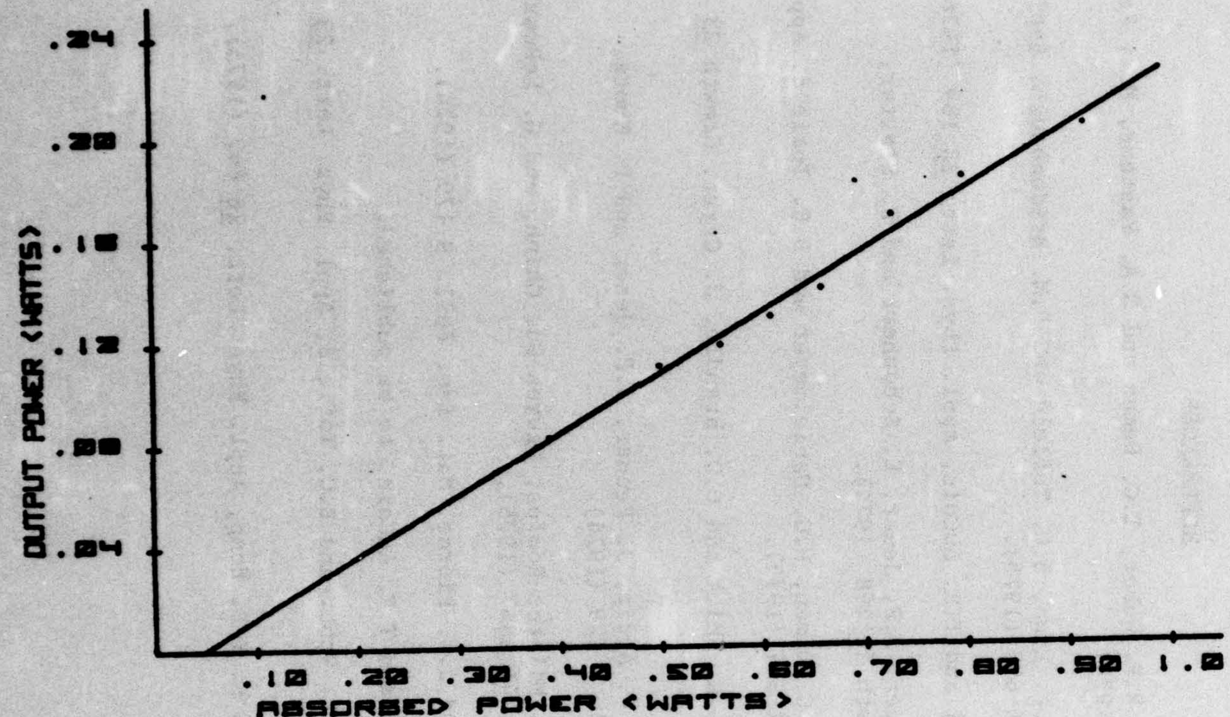


Figure 5. Laser output power of $Nd_{0.9}Y_{0.1}P_5O_{14}$, 2.2 mm thick, as a function of absorbed power using pulsed excitation and a 0.1% duty factor.

REFERENCES

1. B.C. Tofield, H.P. Weber, T.C. Damen and G.A. Pasteur, Mat. Res. Bull. 9 435 (1974).

2. H.P. Weber, P.F. Liao, B.C. Tofield and P.M. Bridenbaugh, Appl. Phys. Lett. 26 692 (1975).

3. J.G. Gualtieri and T.R. AuCoin, Appl. Phys. Lett. 28 189 (1976).

4. H.G. Danielmeyer, J.P. Jeser, E. Schonherr and W. Stetter, J. Cryst. Growth 22 298 (1974).

5. H.P. Weber, T.C. Damen, H.G. Danielmeyer and B.C. Tofield, Appl. Phys. Lett. 22 534 (1973).

6. D.C. Miller, L.K. Shick and C.D. Brandle, J. Cryst. Growth 23 313 (1974).

7. K.R. Albrand, R. Attig, J. Fenner, J.P. Jeser and P. Mootz, Mat. Res. Bull. 9 129 (1974).

8. J.P. Budin, A. Milatos-Roufos, Nguyen Duc Chinh, and G. LeRoux, J. Appl. Phys. 46 2867 (1975).

9. H. P-P, Hong and J.W. Pierce, Mat. Res. Bull. 9 179 (1974).

10. J.G. Gualtieri and T.R. AuCoin, to be published.

11. T.C. Damen, H.P. Weber and B.C. Tofield, Appl. Phys. Lett. 23 519 (1973).

12. S.R. Chinn and H. Y-P, Hong, Appl. Phys. Lett. 26 649 (1975).